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Research Article

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Assessment of Artificial Ornamental Stone Characteristics Produced from Limestone Quarries Waste and Epoxy Resin

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Abstract Ornamental stones industry produces huge amounts of different types of wastes. It can be presented during quarrying (sometimes due to its worth blockability) and / or during sawing which produces large amounts of dust. These wastes may cause great environmental and healthy hazards. Recently, many studies aim to reuse quarries waste to increase their economic values through producing artificial ornamental stones (AOS). AOS is a glazed surface characterized by very low porosity and stains resistance. Also, AOS can be more durable than natural quarried marble .It is also more resistant to stains, wear and damaging effects of house hold chemicals. In this study, AOS plates were produced using two different limestone quarry wastes and epoxy resin. The casted specimens were tested for, physico-mechanical, thermal conductivity, thermo Gravimetric analysis (TGA/Dr.TGA), Fourier-Transform infrared Spectroscopy (FTIR) as well as its durability against salt crystallization and color stability with temperature rising. The produced AOS presented properties comply with values of natural ornamental stones applied in civil construction.

Keywords artificial stone, waste, recycle, epoxy/resin, physico-mechanical

1. Introduction

Marble is a metamorphic rock produced from limestone by pressure and heat in the earth's crust due to geological processes. Commercially marble is using to describe all ornamental stones talking a polished surface regardless their geological origin. Marble is using as an ornamental stone in decoration of engineering building units, for flooring and counter top material in high-end homes for its beauty and elegance. However, even though it is very durable, resistant to scratch and heat, it has other inherent less desirable characteristics. They are naturally porous and prone to staining by oils, acids and some cleaning products, especially if they are not properly sealed or resealed periodically. It also contains tiny pits and natural fissures that may appear to be cracked. The main disadvantages of ornamental stones are the extraction process, whereas 30% of the stone goes to scrap because of being smaller in size and/or being irregularly shaped. Millions of tons of these stone wastes are produced every year during extraction, around the world which leads to significant environmental hazards. Environmental problems have been reported in China due to waste disposal procedures both on-site and off-site the quarry premises [1]. Also, dust produced from sawing of the artificial stone may lead to healthy problems regarding to respiratory systems of workers and inhabitation. Without treatment or recycling, the waste stone sludge would cause environmental pollution [2]. Recycling and reusing of the waste stone fragments and sludge in different applications such as manufacturing concrete [3-4], bricks [5-7], ceramic [8, 9], artificial aggregates [10-13] and asphalt [14-15] as well as stabilizing agriculture soils [16] and water treatment [17-18] have been studied by many researchers. Thus, recycling and reuse of ornamental stone wastes for the development of AOS can be technically economic and environmentally viable, minimizing the amount of wastes disposed in environment, while incorporating economic value to residue and be able to create new job [19]. The ornamental stone wastes can be reused instead of being deposited in the environment [20]. Currently, due to the poor quality of natural stones, short-term adhesive materials in the facade of buildings, high moisture absorption, low resistance, few mining resources, and environmental issues, consumers are looking for stones with superior strength and quality. AOS tiles are more durable than natural quarried one. AOS is characterized by its glazed surface with very low porosity, which makes it resistant to the stains that often occur in the kitchen (oil, coffee, etc.). Also, another advantage of AOS is that it can be dyed to match the color of interior design. The present work aims to produce and investigate properties of AOS fabrication by residue incorporation from two limestone quarries with epoxy resin. Epoxy resins (ER) are very useful substances as polymeric matrix system for developing such new composite materials. So, wastes obtained from quarries can be reused instead of being deposited in the environment.

2. Material and Methods

2.1. Location of Sample Site

The wastes of limestone were used in this study were collected from two quarries located along El korymat - El Zafarana road Southeast Cairo. It is located in Eastern Desert, Egypt. The first limestone quarry (Ko) is located at latitude: 29^0 03' 34" N and longitude 31^0 33' 58" E (about 115 Km Southeast Cairo). The other quarry (Sa) is black limestone quarry which is located about 334 km Southeast Cairo. It is located at latitude: 28^0 54' 12" N and longitude E 32^0 19' 19" E (Fig.1).

2.2. Sample Preparation

Samples were collected from the quarries waste (Fig. 2) were crushed and added to epoxy resin diglycidyl ether of bisphenol A (DGEBA) with density: 1,16 g/ml and molar mass: 340,41 g/mol. In addition, Tetraethylenepentamine amine (TEPA) was used as hardener with density: 0.99 g/ ml and molecular weight: 189.31. The studied limestone wastes were crushed into smaller size and sieved to reach a size ranges from 1.18mm to 2. 36 mm, then it mixed together by proportion 50% to 50% by weight. After manually mixing of the mixture with stirrer in a container, the epoxy/resin was used in the proportions indicated by the manufacturer in order to provide the best performance. Then the mixtures were poured into various silicon rubber moulds (using vibrator table) having a shape similar to the final required product shape. The products were left for five to six hours of optimum curing time (in room temperature). The using of different color limestone wastes (Ko & Sa) contributes to give similar appearance of the natural granitic rocks. The fabrication process in which involved in manufacturing of AOS is shown in Figure 3.

Figure 1: Location map of the selected limestone quarries sample

Figure 2: Field photographs showing some sites of wastes produced from limestone quarrying (A: limestone waste. B: black limestone waste)

Figure 3: Photographs showing the steps of artificial ornamental stone production (A: Mixing of the two limestone waste samples together then with epoxy/resin, B: various molds and casting, C: the produced artificial ornamental stones)

2.3. Physico-mechanical Properties

Bulk density, water absorption, apparent porosity and modulus of rupture were measured according to ASTM [21], [22], [21] and [23]; respectively. Compressive strength was tested according to ASTM [24]. The compressive load was determined using a loading rate 10KN/ min on RMU TESTING Equipment, 57-2400 Bergamo (Italy) with maximum force 1500 KN. Abrasive wear was determined using Wide Wheel abrasion test (capon, [25].)

2.4. Mineralogical Composition and Chemical Analyses

The mineralogical composition of the studied limestone waste has been investigated using X-ray diffraction (XRD) X-ray model X´Pert ProPhillips MPD PW 3050/60 X-ray diffractometer. Chemical analysis of major oxides was determined for the studied waste using X-ray Fluorescence (XRF) (Phillips PW 1400 Spectrometer, Holland).

2.5. Durability

The most common weathering actions that affect stone durability are: (1) Moisture, which may cause organic deterioration; (2) Frost action which causes cracking, flaking and spalling; (3) Salt decay caused by the salt contained in the stone itself and the acid rain; (4) chemical reactions caused by rain and carbon dioxide (CO_2) which may affect stones that contain calcium, magnesium and sodium.

2.5.1 Salt Crystallization

In this study, the durability of AOS was determined through its resistance to two types of salt crystallization ($NaNO_2$ & $Na_2SO_4.10H_2O$). Four cubes of AOS (5 cm* 5 cm* 5 cm) were cleaned and dried till constant weight at 75ºC. The original dried weight was recorded. The cubes were totally immersed in two beakers contain solutions of 14% $NaNO_3$ & $Na_2SO_4.10H_2O$, respectively for two hours. Then cubes were dried in the oven at 75 ºC for 22 hours. The samples were left to cool down to room temperature and the weight was recorded. The cubes were subjected to 21 cycles.

4.5.2. Color Stability with Rising Temperature

AOS samples were heated at different temperature to notice the specific temperature at which stone loses its color.

2.6. Determination of Thermal Conductivity Coefficient

The coefficient of thermal conductivity in the present study was calculated according to [27] using heat Flow Meter (HFM 436 Lambada series, Netzsch).

2.7. Thermo Gravimetric Analysis (TGA/Dr.TGA)

This technique is designed to detect any thermal changes accompanying chemical or structural transformation during the heating of a particular component. As confirmatory tools, differential thermal (DTA) and thermo-gravimetric (TGA) analyses were used for the studied samples. The thermal analyses were carried out using computerized DT.50 thermal analyzer (Shimadzu Co., Kyoto, Japan). The heating rate was 10°C/min. The heating temperature was up to 1000°C for DTA and TGA under nitrogen atmosphere (20 ml/min). A constant condition of sensitivity (± 5 mg) was applied for the experiment at Thermal Laboratory of Housing & Building Research Center (HBRC).

2.8. Fourier Transformed Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to study the limestone wastes sample, epoxy and AOS. The samples were ground to powder, mixed with potassium bromide, and a thin film was prepared at room temperature. The potassium bromide was used as the background. The scanning spectrum was recorded in the wave number interval between 4000 cm^{-1} and 400 cm^{-1}.

3. Results and Discussion

3.1. Physico-Mechanical Properties

Table (1) shows the measured physico-mechanical properties of the produced AOS. The recorded average bulk density of the produced AOS was 2g/cm^3, which is 20% lower than those reported for the compound marble manufacturers that inform density values range between 2.4 and 2.5 g/cm^3. The recorded density value found in this research is in agreement with the literature, with no significant changes in results. With respect to the measured water absorption value of the produced AOS was found of 0.1 %. This value is similar to those reported by [28] which range from 0.09 to 0.40%. According to Chiodi and Rodriguez [29], a value below 0.1% has a very high quality. Also, Chiodi and Rodriguez [29] reported that high quality materials should be less than 0.5%. The low porosity was due to the good adhesion of the resin to the particles, and also due to filling the voids provides homogeneity to the system. The measured apparent porosity of the produced AOS was 0.26%.

Table 1: Physico-mechanical properties of produced AOS

Bulk density (gm/cm^3)	2	Compressive strength (MPa)	52
Water absorption (%)	0.13	Modulus of Rupture (MPa)	17
Apparent porosity (%)	0.26	Abrasive wear (mm)	16

The measured dry compressive strength is about 52 MPa (530 Kg/cm^2). It passed the minimum requirement of the natural marble according to [30] and is slightly lower than the requirement of high density limestone according [31]. In the bending flexural strength test at three points, modulus of rupture value is 17 MPa which is greater than the minimum expected for natural marble regulated by [30] that should be greater than 7 MPa. It also exceed the values of high density limestone [31] and granite [32] which are 7, 10.83 Mpa, respectively. The average values of abrasion resistance were 16 mm. it is locates in the intensive zone (≤24mm) according to [25].

3.2. Mineralogical Composition and Chemical Analysis

XRD analysis was conducted on the collected limestone waste samples (Ko & Sa) to identify their mineralogical composition. The obtained results (Fig.4) revealed that both of these waste samples are composed essentially of calcite mineral.

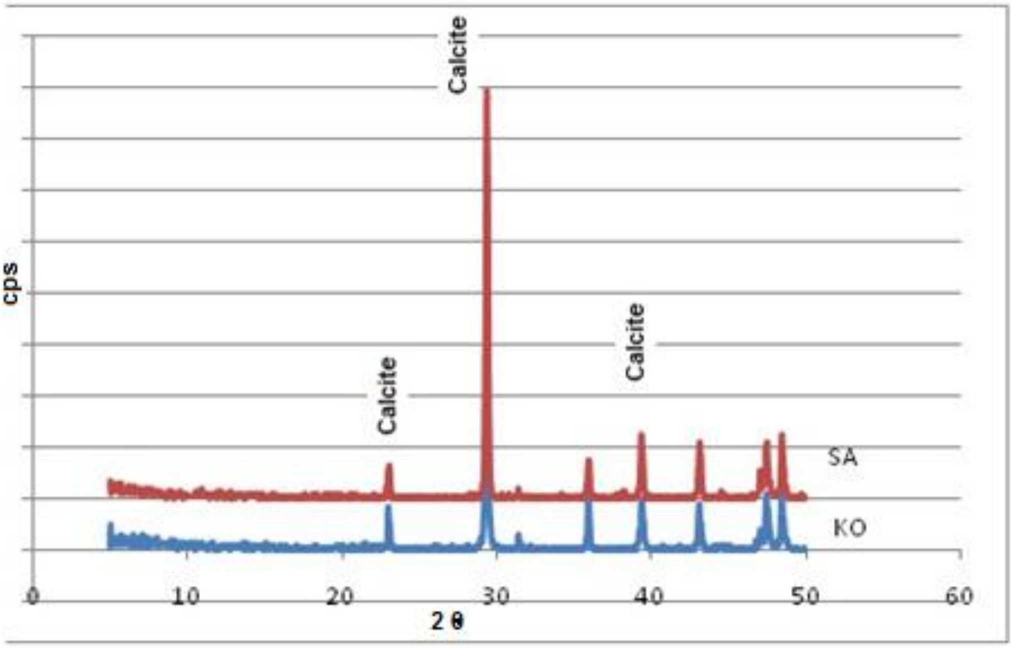


Figure 4: XRD patterns of the studied limestone waste samples

The chemical composition of the studied limestone waste samples (Table.2) was determined by the XRF analysis. The recorded results revealed that CaO is the most dominant major oxide in the studied samples. On the other side, other major oxides are rare where as they are dominated by SiO_2. Moreover, noticeable MgO oxide was detected in the SA sample.

Table 2: Chemical composition of limestone waste samples

Sample	CaO	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Fe_2O_3	Na_2O	K_2O	SrO	L.O.I	total
Ko	54.1	0.19	0.16	1.35	0.02	0.60	0.05	--	--	0.02	43.47	99.96
Sa	50.4	1.78	0.69	4.93	0.10	0.17	0.26	0.19	0.11	--	41	99.63

3.3. Salt Crystallization

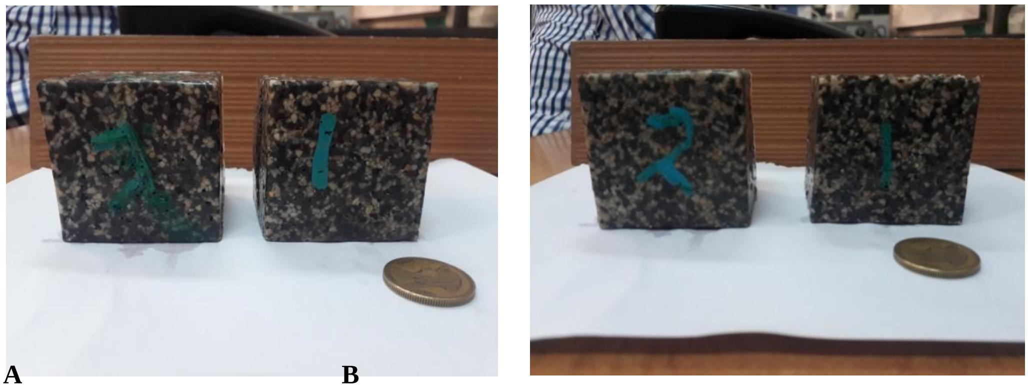
The average weight loss of the produced AOS samples were calculated after 21 cycles (Table 3). There is no any visible deterioration evidences (edges and corners degradation, cracks, shuttering …) were observed in the tested cubes (Fig. 5). The studied AOS samples can be classified similar to the limestone durability classes reported by [33] where, they fall into class A (ΔM % ≤ 1). Based on its durability class (A), the studied artificial stone can be used in exposure zones from first to fourth of a building under different environmental conditions according to [33].

Table 3: The weight loss due to salt crystallization for different solutions

$NaNO_3$		$Na_2SO_4.10H_2O$	
ΔM %	-0.06	ΔM %	-0.08

3.4. Color Stability with Temperature

The produced AOS samples were heated gradually for one hour with temperature ranging from 10 to 200 ^{0}C. This was done to observe any color change of the colorless epoxy, where as this color was started to change at 200 ^{0}C and was not able to keep its casting color appearance (Fig. 6).



A **B**

Figure 5: The investigated AOS samples after complete 21 cycles in A & B solutions (A:$NaNO_3$ – B: $Na_2SO_4.2H_2O$)

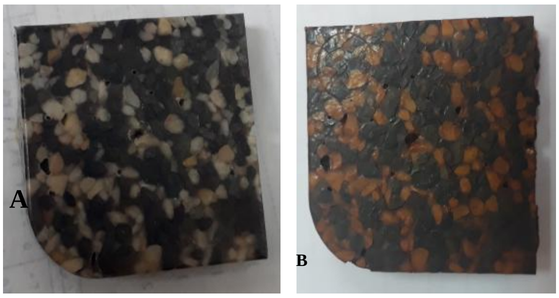


Figure 6: Color variation in the produced AOS samples (A: before heating, B after heating to 200ºC for an hour)

3.5. Thermal Conductivity

A thermal conductivity assigned to a material that exhibits thermal transmission by several modes of heat transfer resulting in property variation with specimen thickness, or surface emittance according to [26]. The obtained results thermal conductivity of AOS sample is 0.16 W/mk which are lower than those of natural marble (0.2 W/mk). The obtained low thermal conductivity result throws the light for the possibility to play role in insulation. Many studies have shown that the thermal conductivity of a porous rock depends mainly on the mineralogical composition, porosity of the rock, presence of fluids filling the pores, and ambient temperature and pressure [34]. Generally, low thermal conductivity of natural stone has advantages especially when using as outside wall cladding material as it increases insulation and thus reduces energy consumption.

3.6. Thermo Gravimetric Analysis (TGA)

The thermo Gravimetric curve (TGA) of the produced AOS sample shows four stages of weight loss (Fig.7). The first stage shows a weight loss of approximately 3.4% at the temperature of about 108 ºC concerning the decomposition of the water. The Differential Thermo Gravimetric (DTG) curve (Fig.7) also confirms this water removal. The second weight loss (12.5%) is corresponds to decomposition of the resin at the temperature of about 311.4 ºC. The third weight loss (10.8%) corresponds to combustion of the remaining epoxy resin under high temperature. Further, it has been observed the final weight loss of approximately 46.2% which can be attributed to the decomposition of the carbonate to oxide.

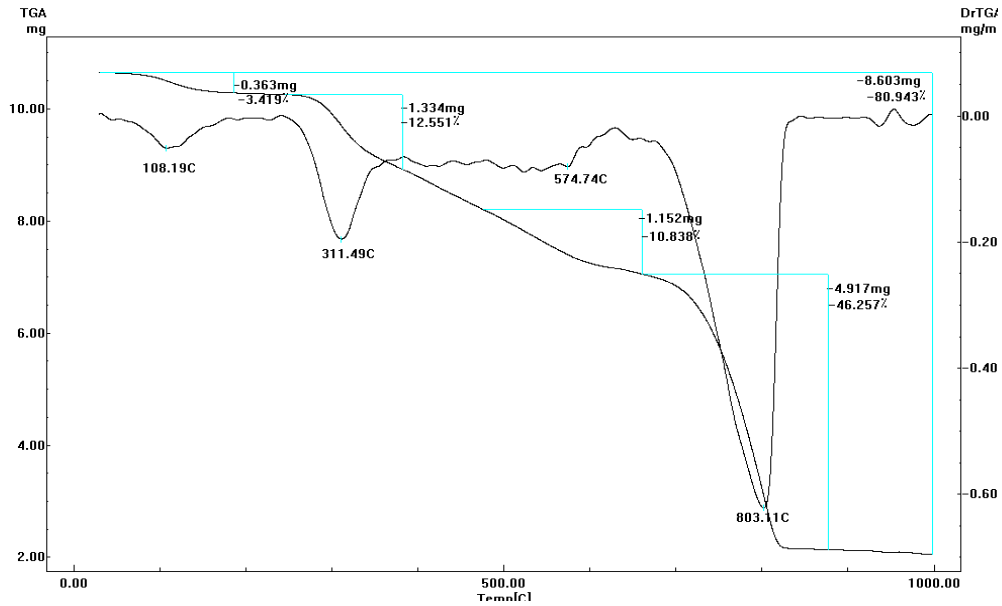


Figure 7: TGA-DTG curves of the produced AOS sample in the temperature range from 10 to 1000 ºC

3.7. Fourier Transformed Infrared Spectroscopy (FTIR)

The FTIR data (Fig.8) give an idea about the molecular structures, chemical bonds present and their strength in the samples. The infrared spectra of limestone wastes samples show that the calcite is the main mineral phase as observed at 711.9 cm^{-1}, 877.1 cm^{-1} and at 1400 cm^{-1} assignable to the CO_3^{-2} group. The spectra of epoxy/ resin show that the different bonds present give information about the properties of the composite and how these bonds can be modified to improve its properties. The results revealed that epoxy is belonging to the glycidyl epoxies family (aromatic epoxy/resin). The band which appeared at 1509 cm^{-1} is corresponding to Stretching C-C of aromatic while band at 1607.4 refer to Stretching C=C of aromatic rings. C-H stretching of terminal oxirane group is observed 3060 cm^{-1}. The broad band at 3375 cm^{-1} is assigned to O-H stretching of hydroxyl groups, revealing the presence of dimers or high molecular weight species. There are bands corresponding to the ether linkage were detected at 1034-1108 cm^{-1}. In addition, there are also bands corresponding to CH_2, CH_3 bending located at 1342-1459 cm^{-1}. Bands at 1182.3 cm^{-1} and 1247 cm^{-1} are corresponding to C-C-O-C-stretching. Spectra of AOS shows less epoxy/ resin bands due to the CO_3^{-2} group broad band of limestone wastes sample which masked many bands of epoxy/ resin. There are bands corresponding to C-H of CH_2, CH aromatic and aliphatic which located at 2871-2961 cm^{-1}.

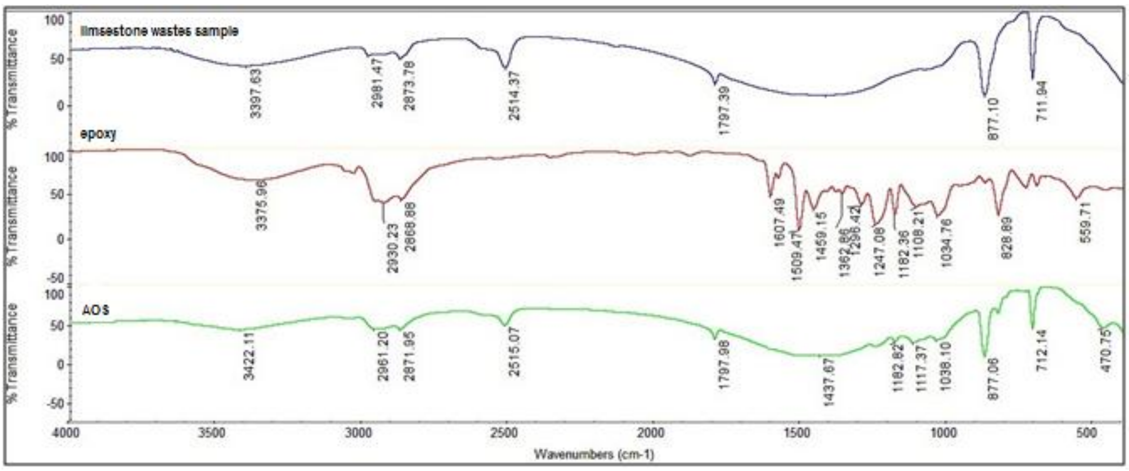


Figure 8: FTIR chart for the limestone wastes sample, epoxy/resin and artificial ornamental stone from 400 to 4000 wavelength (cm^{-1})

4. Conclusion

The use of this epoxy resin together with limestone quarry wastes produce a high-performance artificial ornamental stone with excellent properties which providing both environmental solutions for waste and benefits economics. The produced artificial ornamental stones have a wide range of using. In addition, artificial stone presents advantages over the natural stone, such as low porosity, low water absorption and considerable mechanical properties. The flexural strength value of the produced AOS was 17 MPa, and its compression value was 52 MPa, such mechanical values are satisfactory. The obtained physical results are also show apparent porosity of only 0.23% and 0.13% of water absorption, demonstrating the high impermeability and quality of the produced AOS. The measured values of hydroscopic properties (bulk density, water absorbance & apparent porosity) for casting artificial were achieved average values better than traditional reference values. For abrasive wear, encourage results were also obtained, it was only 16 mm which shows great resistance for abrasion. The results indicated thermo-gravimetric mass loss behavior as expected for artificial stones, for the artificial stone (produced from limestone wastes) was a decomposition of $CaCO_3$ into oxides Vibro-vacuum compression machine is recommended to use for producing artificial ornamental stone in the future studies where, it will allow a better adhesion between the epoxy/resin and the limestone wastes providing better mechanical properties for the produced artificial stone.

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